Trace metals and Mo isotopic fractionation in Skagerrak sediments – effects of different oxygen conditions

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Chemicals and labware

Ultrapure water for trace metal analysis (>18.2 MΩ cm) was obtained from an ultrapure water system consisting of an Elix 3 module (Merck Millipore, Germany), a Milli-Q element module (Merck Millipore, Germany) and a Q-POD element (Merck Millipore, Germany). Analytical grade HNO3 (65% w/w, Fisher Scientific, Germany) and analytical grade HCl (30% w/w, Carl Roth, Germany) were further purified by double subboiling in perfluoralkoxy-polymer (PFA)-subboling stills (DST4000 & DST-1000, Savillex, USA), operated under clean room conditions. HBF4 (38% w/w, Chem-Lab, Belgium) was used in ultra-pure quality for sample digestion without any further purification. The *Digi*TUBE™s (50 mL or 100 mL, SCP Science, Canada) were rinsed three times with ultrapure water, filled with HNO3 (w = 1.3%) and allowed to stand for at least one week. Before use, they were rinsed three times with ultrapure water again. Only for $\delta^{98/95}$Mo analysis, the *Digi*TUBE™s were used from the bag without further cleaning. Centrifuge tubes (PP, 15 mL Labcon®, USA; 50 mL Greiner Bio-one, Germany) were used without rinsing.

Sediment and porewater sampling

The sediment cores were taken with a Multicorer (Oktopus Kiel) equipped with transparent acrylic (Poly(methyl methacrylate)) core liners (10 cm inner diameter, 60 cm length). Directly after sampling, the cores were cut into 1 cm slices, stored in pre-cleaned PP containers (120 mL, ratiolab, Germany) and cooled (4 °C) until the start of the incubation experiment. Sediments for analysis of depth profiles were sliced into *Digi*TUBE™s (100 mL, SCP Science, Canada) and frozen (-20 °C) immediately. For porewater sampling, the same core liners as for sediment sampling were used but these were prepared with holes along the length of the core, which were sealed with tape during sampling. Directly after sampling, air-tight rhizon samplers (0.15 µm pore size; Rhizosphere Research Products, Netherlands) attached to a syringe (10 mL, B.Braun, Germany) were pierced through the tape at the respective depths. After all rhizons were installed, the syringes were drawn up simultaneously and the applied vacuum collected the porewater. After sampling, the porewater was filled into PP vials, acidified with HNO_3 (to w=1.3%) and frozen until analysis. The air-tight rhizons already ensure filtration of the samples without air contact.

Sample analysis

The freeze-dried sediments were homogenized by grinding in a planetary mill (15 min, 300 rpm, Retsch, Germany). For trace element analysis, 50 mg aliquots were digested with a mixture of 5 mL HNO_3, 2 mL HCl and 1 mL HBF_4 in TFM digestion vessels (35 mL, CEM Corp., Germany). The digestion was done at 180 °C for 360 min with a MARS 6 microwave (CEM Corp., Germany). After digestion, the samples were transferred into *Digi*TUBE™s and diluted to 50 mL total volume with ultrapure water. The sediment digests were measured on an ICP-MS/MS (Agilent 8800, Agilent Technologies, Japan) with He, H_2 and N_2O as reaction gases. The calibration was prepared daily from custom-made multi-element standards (traceable to NIST standards; Inorganic Ventures, USA) and ranged between 0.1 µg L^{-1} and 100 µg L^{-1}. An internal standard (Ir, Rh) was dosed online to every sample to allow for drift correction if necessary. Measured isotopes, blanks and recoveries of reference material (BCR-2, USGS, USA; GBW07311, CNRM, China) and repeatedly measured in-house multi-element standard solution (250 µg L^{-1} for Fe

and As, 25 µg L^{-1} for all other elements) are given in the supplementary material (Table S2). Further information on the method is given elsewhere (Klein et al., 2021; Pröfrock & Prange, 2012; Zimmermann et al., 2020). Porewater samples were diluted 1:10 with ultrapure water and measured with the same method as the sediments with two certified reference materials to account for the decreased salinity of the diluted samples (CASS-6, SLRS-6; NRC, Canada) and the in-house multi-element standard solution (250 µg L^{-1} for Fe and 25 µg L^{-1} for all other elements; Table S4). The dissolved trace element concentrations in the incubated water were analyzed online with a sea*FAST* SP2 (Elemental Scientific, USA) coupled to a collision cell ICP-MS (Agilent 7900, Agilent Technologies, Japan) or an ICP-MS/MS (Agilent 8900, Agilent Technologies, Japan), operated in single-quadrupole mode. He/H_2 (4.0 mL min^{-1}, 0.5 mL min^{-1}) were used as cell gases. Measured isotopes, blanks and recoveries of a seawater reference material (NASS-7, NRC, Canada) as well as a repeatedly measured in-house multi-element standard solution (250 ng L^{-1} or 2500 ng L^{-1} for Fe, 25 ng L^{-1} or 250 ng L^{-1} for all other elements) are given in Table S3, for further information on the used method, see Ebeling et al. (2022); Przibilla et al. (2023).

$\delta^{98/95}$Mo analysis

For Mo isotope analysis, the sediment digests or water samples (equivalents of 75-200 ng absolute Mo) were dried down in a *Digi*TUBE™. Porewater samples were pooled for several depths to yield sufficient sample volume. Additionally, IAPSO standard sea water and SRM3134 (NIST, USA) were prepared in the same manner to validate the method for water analysis and GBW07311 (CNRM, China) and BCR2 (USGS, USA) to validate- the sediment analysis. At the university of Calgary, the sediment and water samples were redissolved in 4 mL or 2 mL 3 mol L^{-1} HNO_3, respectively. A $^{92/98}$Mo double spike was added and the sample was dried down in an evaporation unit (*Digi*Prep™ Jr, SCP Science, Canada). To homogenize the double spike and prepare the sample for ion exchange, the sample was sequentially redissolved and dried down in 4 mL HCl (4 mol L^{-1}) and 100 µL HCl (concentrated) before redissolution in 4 mL 4 mol L^{-1} HCl. For the ion exchange, Analytical Grade Anion Exchange Resin (1x8, 100-200 mesh, Chloride form, Eichrom, USA) and Cation Exchange Resin (100-200 mesh, 50Wx8, Hydrogen form, Eichrom, USA) were used. The resins were rinsed with 5 mol L^{-1} HNO_3, ultrapure water and 4 mol L^{-1} HCl directly before use. 1 mL glass columns were used for ion exchange. More information on the ion exchange procedure is available in Wieser et al. (2007).

Mo isotope-amount ratios were measured at the University of Calgary using a Neptune MC ICP-MS (Thermo Fisher Scientific, Germany) operated in low mass resolution mode. Samples were introduced with an ESI SC2-DX autosampler (Elemental Scientific, USA) through a Teflon spray chamber (Elemental Scientific, USA) into a quartz torch. Eight Faraday cups (10^{11} Ω resistors) were used to measure the ion beams of ^{91}Zr, ^{92}Mo, ^{94}Mo, ^{95}Mo, ^{96}Mo, ^{97}Mo, ^{98}Mo, ^{100}Mo. Sample measurements consisted of one acquisition block with 20 measurements. Data reduction of the double spike was done with a custom-written python script (Mayer & Wieser, 2014; Rudge et al., 2009). The results for the reference materials are given in Table S5. From the SRM3134 (NIST, USA) standard, the $\delta^{98/95}$Mo ratio was calculated.

Calculation of trace metal fluxes in Figure 6

The fluxes of Cd, Cu, Ni and Pb in the incubations were calculated from the metal concentration at the start (c_{start}) and end (c_{end}) of the incubation experiment, i.e. at month 0 and month 12 (Table S7) The difference between both concentrations was multiplied with the incubated water volume (V; 0.065 L for aerobic, 0.120 L for anaerobic incubations) to obtain the absolute mass of released metal and divided by the mean of the incubated sediment mass per incubation triplicate for the last time step (m_{sed}; Table S1), leading to the following equation:

$$flux = \frac{(c_{end} - c_{start}) * V}{m_{sed}}$$

The uncertainty of the flux was calculated as expanded uncertainty ($U(k=2)$) from the errors of the individual variables.

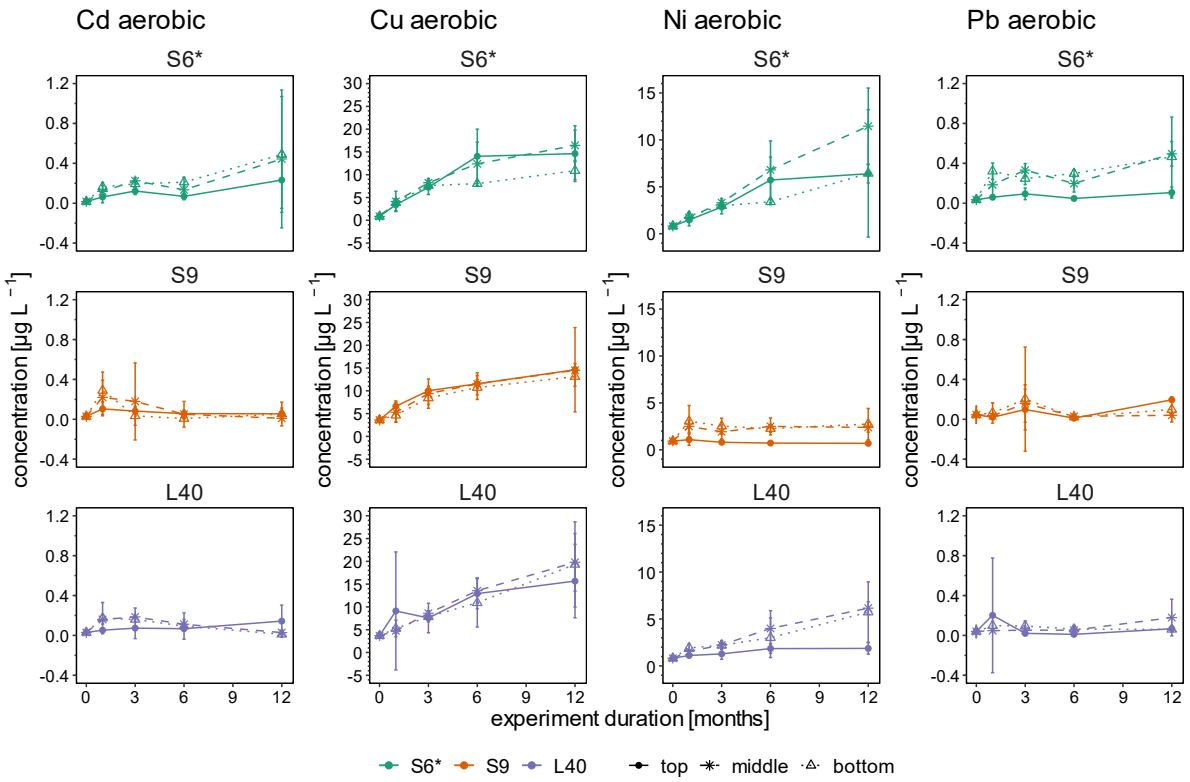

Figure S1 Dissolved concentrations of Cd, Cu, Ni and Pb for aerobic incubations of top (circle, solid line), middle (star, dashed line) and bottom (triangle, dotted line) sediments from stations L40 (purple), S6 (green) and S9 (orange). Error bars correspond to the expanded uncertainty U(k=2). If error bars are not visible, they are smaller than symbol size.*

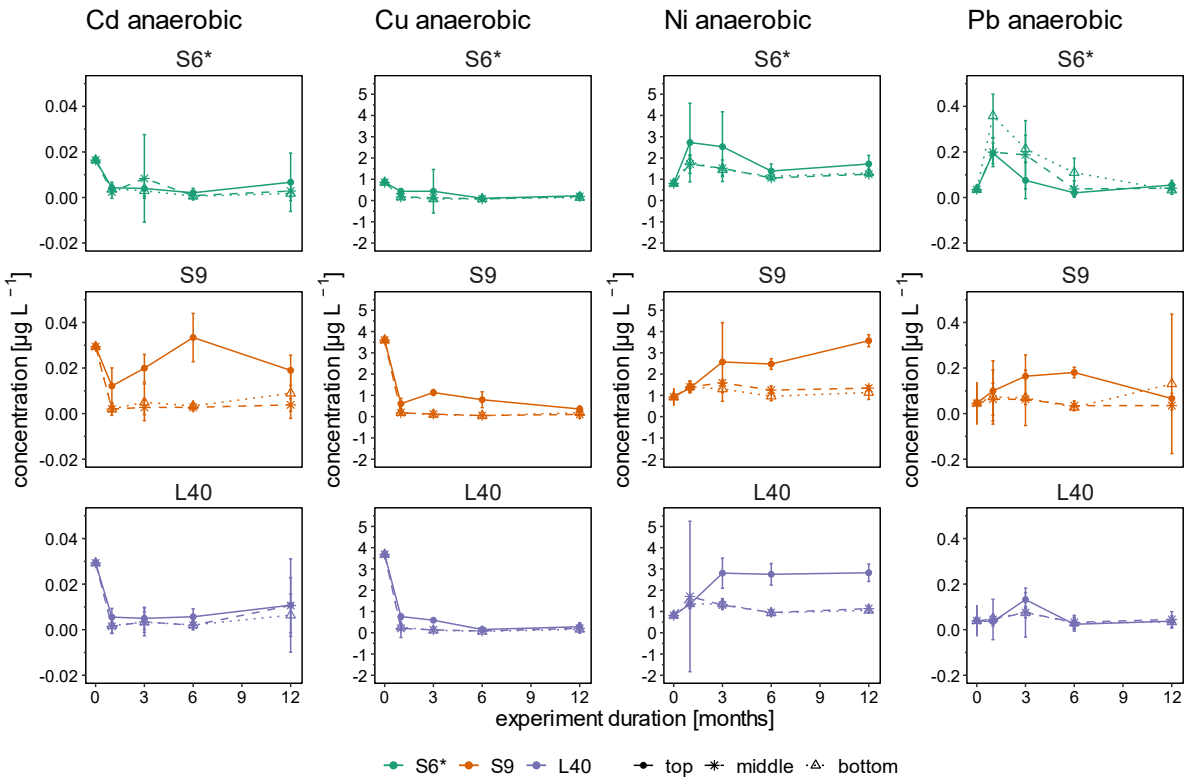

Figure S2 Dissolved concentrations of Cd, Cu, Ni and Pb for anaerobic incubations of top (circle, solid line), middle (star, dashed line) and bottom (triangle, dotted line) sediments from stations L40 (purple), S6 (green) and S9 (orange). Error bars correspond to the expanded uncertainty U(k=2). If error bars are not visible, they are smaller than symbol size.*

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